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Research paper

Getters for improved technetium containment in cementitious waste forms

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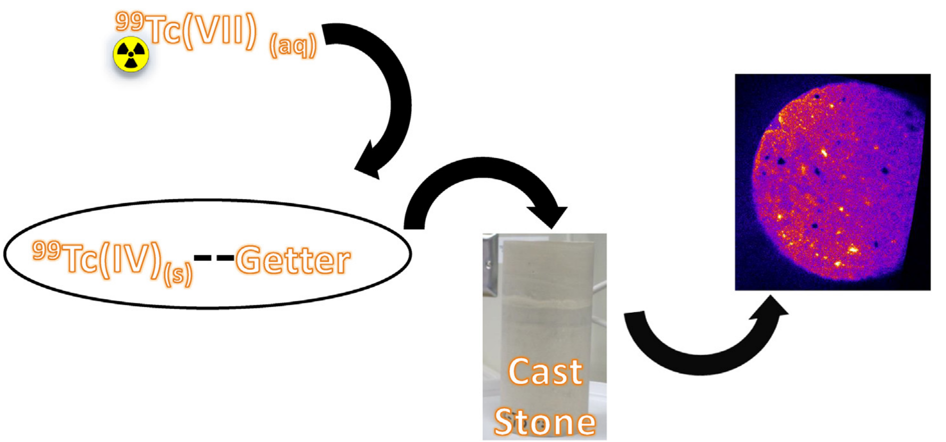
HIGHLIGHTS

- KMS-2 and Sn(II) apatite were used as Tc getters in cementitious waste forms.
- KMS-2 had higher capability of Tc removal from simulated low-activity waste.
- Addition of KMS-2 (<0.08 wt% of overall waste form)improved Tc retention.
- Tc identified to remain associated with getter within the cured Cast Stone waste form.
- Improved retention by KMS-2 linked to generation of Tc(IV)-sulfide species.

GRAPHICAL ABSTRACT



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ABSTRACT

A cementitious waste form, Cast Stone, is a possible candidate technology for the immobilization of low activity nuclear waste (LAW) at the Hanford site. This work focuses on the addition of getter materials to Cast Stone that can sequester Tc from the LAW, and in turn, lower Tc release from the Cast Stone. Two getters which produce different products upon sequestering Tc from LAW were tested: Sn(II) apatite (Sn-A) that removes Tc as a Tc(IV)-oxide and potassium metal sulfide (KMS-2) that removes Tc as a Tc(IV)-sulfide species, allowing for a comparison of stability of the form of Tc upon entering the waste form. The Cast Stone with KMS-2 getter had the best performance with addition equivalent to ~0.08 wt% of the total waste form mass. The observed diffusion (D_{obs}) of Tc decreased from $4.6 \pm 0.2 \times 10^{-12}$ cm^2/s for Cast Stone that did not contain a getter to $5.4 \pm 0.4 \times 10^{-13}$ cm^2/s for KMS-2 containing Cast Stone. It was found that Tc-sulfide species are more stable against re-oxidation within getter containing Cast Stone compared with Tc-oxide and is the origin of the decrease in Tc D_{obs} when using the KMS-2.

1. Introduction

The environmental risk associated with technetium-99 (Tc) release from nuclear waste forms is high due to its long half-life

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Table 1
Composition of the LAW Simulant utilized in Cast Stone formation.

Compound	Amount for 1 L (g)	Anion/Cation	Measured Concentration (g/L)	Concentration (mol/mol Na)
DDI	200 mL	Na^+	153.33	1.000
KNO_3	4.60	Al^{3+}	11.75	0.065
NaCl	3.04	Cl^-	3.47	0.015
NaF	1.64	$NO_3{}^-$	140.00	0.339
Na_2SO_4	15.70	$NO_2{}^-$	37.04	0.121
$Al(NO_3)_3{\cdot}9H_2O$	148.74	$SO_4{}^{2-}$	11.58	0.018
NaOH (50% soln)	289.12	K^+	2.08	0.008
$Na_3PO_4{\cdot}12H_2O$	24.71	$PO_4{}^{3-}$	1.47	0.002
$NaC_2H_3O_2$	6.64	Free OH^-	35.39	0.312
Na_2CO_3	37.89			
DDI	100 mL			
$Na_2Cr_2O_7{\cdot}2H_2O$	2.31			
DDI	100 mL			
$NaNO_3$	74.03			
$NaNO_2$	50.68			
DDI	100 mL			

Table 2
Composition of the simulated Hanford VZPW leachant..

VZPW Recipe			
Order	Molarity (mol/L)	Reagents	g/L
1	0.012	$CaSO_4{\cdot}2H_2O$	2.07
2	0.0017	NaCl	0.10
3	0.0004	$NaHCO_3$	0.03
4	0.0034	$NaNO_3$	0.29
5	0.0026	$MgSO_4$	0.31
6	0.0024	$MgCl_2{\cdot}6H_2O$	0.49
7	0.0007	KCl	0.05

Adjust pH to 7.0 (±0.2) with sodium hydroxide or sulfuric acid dependent on initial pH.

of 213,000 years and its high mobility in subsurface environments [1]. In oxidizing environments Tc primarily exists in an oxyanion form, pertechnetate ($Tc(VII)O_4{}^-$). $TcO_4{}^-$ exhibits limited adsorption onto many common minerals including silicates, carbonates, phosphates and sulfates (e.g. biotite, apatite, dolomite and gypsum) from the aqueous phase [2,3], influenced heavily by its oxidation state [4]. As a result, $TcO_4{}^-$ in groundwater will migrate rapidly under oxic conditions, irrespective of the biogeochemistry, climate, and physical characteristics of the site [5,6].

Vitrification to produce a borosilicate glass is a common technology for immobilization of radioactive liquid wastes, owing to the long-term chemical stability of glass. However, vitrification requires high temperatures (>1000 °C) and certain radionuclides, such as Tc [7], are highly volatile at such temperatures. The result is limited incorporation of volatile radionuclides into the final glass waste form and generation of secondary waste streams that require additional immobilization and management. The challenge of immobilization of liquid nuclear wastes containing volatile radionuclides, such as Tc, is best exemplified by the environmental clean-up mission currently ongoing at the U.S. Department of Energy (DOE) Hanford site. Fifty-six million gallons of the chemically complex, radioactive waste currently remain stored in 177 storage tanks at the site [8]. A significant Tc plume exists in the subsurface [9] resulting from both the tank leaks and purposeful disposal to shallow cribs and trenches. Current management plans for the Hanford tank wastes call for separation into high-level (high radioactivity and low volume, HLW) and low-activity (high volume and moderate radioactivity, LAW) waste streams. The LAW waste forms, from both tank waste treatment and secondary waste streams will be disposed of on-site at the Integrated Disposal Facility (IDF).

Cementitious waste forms (CWF) present suitable characteristics for treating Tc containing liquid wastes as their fabrication temperatures are below the volatility point of Tc. CWFs are currently used for the immobilization of low level liquid wastes at global waste treatment sites for low level wastes [10,11] and under consideration as an immobilization technology in several countries [12–15]. Cast Stone, a Hanford site specific CWF comprised of a dry mix of 47 wt% blast furnace slag (BFS), 45 wt% fly ash (FA) and 8 wt% ordinary Portland cement (OPC), is currently being considered as a possible candidate waste form to provide additional LAW immobilization capacity [16–19]. The Cast Stone composition is based from the saltstone cementitious waste form (45 wt% BFS, 45 wt% FA and 10 wt% OPC) utilized for solidification of low level radioactive wastes at the Savannah River Site in South Carolina since the early 1990s [20–22]. The presence of BFS in the waste form is important as it provides reducing capability to slow Tc release. In testing of CWF with and without the presence of BFS, it was found BFS presence led to large improvements in Tc retention due to the BFS generating Tc(IV) species [23,24]. Other candidate waste forms include Ceramicrete [25] and DuraLith geopolymer [26].

From initial investigations of these waste forms, it was determined that Cast Stone had promising properties for retention of Tc [16]. It was concluded that retention of radionuclides by the Cast Stone, and CWFs in general, could be improved through the inclusion of materials which can selectively sequester radionuclides or contaminants of interest in both the liquid state and final waste form, termed getters [27].

A range of getter materials that sequester Tc from aqueous media has been investigated including metal oxides [28], nanomaterials [29,30], carbon-based materials [31], aluminophosphates [32], and resins [33,34]. Many of these materials showed promise for the sequestration of Tc from chemically inert aqueous environments at circumneutral pH and with low ionic strengths [35–37]. However, a drastic drop in performance was observed with many Tc getters upon moving to extreme chemical environments with high ionic strength, high/low pH and presence of competitive redox-active species. These more extreme conditions are relevant to sequestration of Tc from LAW because it has a high pH (>13), high ionic strength (between 5 M and 8 M Na), and contains high levels of redox-active species, such as Cr(VI) and $NO_3{}^-$. Two getter materials have recently shown high promise for the sequestration of Tc from chemically complex liquid waste environments, including LAW: Sn(II)-treated apatite (Sn-A) [38] and layered potassium metal sulfide (KMS-2) [39]. Although the mechanisms vary, both the Sn-A and KMS-2 sequester Tc from solution through reduction of Tc(VII) to Tc(IV). The Sn-A sequesters Tc(VII) as a Tc(IV)-oxide and KMS-2 sequesters Tc(VII) as a Tc(IV)-sulfide.

Here, we present the process of fabrication, testing and thorough characterization of Cast Stone containing either Sn-A or KMS-2 as